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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵: C08L 25/06, 71/12, 53/02	A1	(11) International Publication Number: WO 94/24206 (43) International Publication Date: 27 October 1994 (27.10.94)
(21) International Application Number: PCT/US94/00790 (22) International Filing Date: 21 January 1994 (21.01.94) (30) Priority Data: 08/050,949 21 April 1993 (21.04.93) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: WESSEL, Thomas, E.; 3001 Lambros Drive, Midland, MI 48642 (US). HUANG, Yi-Bin; 5405 Wallbridge Lane, Midland, MI 48640 (US). THILL, Bruce, P.; 2103 Burlington Drive, Midland, MI 48642 (US). (74) Agent: DELINE, Douglas, N.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: IMPACT MODIFIED SYNDIOTACTIC VINYLAROMATIC POLYMERS (57) Abstract An impact modified syndiotactic vinylaromatic polymer comprises: A) from 25 to 90 parts by weight of a syndiotactic, vinylaromatic thermoplastic resin, B) from 1 to 50 parts by weight of a rubbery, impact absorbing, domain forming polymer, having a melt flow rate, Condition X (315 °C, 5.0 Kg) from 0 to 0.5 g/10 min, C) from 0.1 to 30 parts by weight of a nucleator for the syndiotactic, vinylaromatic thermoplastic resin, D) from 0 to 90 parts by weight of a reinforcing agent, and E) from 0 to 90 parts by weight of a polyarylene ether or polar group modified polyarylene ether.		

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IMPACT MODIFIED SYNDIOTACTIC VINYLAROMATIC POLYMERS

The present invention relates to syndiotactic vinylaromatic polymer compositions containing impact modifiers. More particularly the present invention relates to such compositions that are further modified to incorporate crystal modifiers and optionally reinforcing aids, and compatibilizers.

In JP-A-1-135868, published May 29, 1989, there are disclosed certain resin compositions containing (a) inorganic fillers and (b) polyphenylene ether type resins including maleic anhydride modified poly(2,6-dimethyl-1,4-phenylene)ether. The resins are useful for electrical parts.

According to the present invention there is provided a composition of matter comprising:

- A) from 25 to 90 parts by weight of a syndiotactic, vinylaromatic thermoplastic resin,
- B) from 1 to 50 parts by weight of a rubbery, impact absorbing domain forming polymer, having a melt flow rate, Condition X (315°C, 5.0 Kg) from 0 to 0.5 g/10 min,
- C) from 0.1 to 30 parts by weight of a nucleator for the syndiotactic, vinylaromatic thermoplastic resin,
- D) from 0 to 60 parts by weight of a reinforcing agent, and
- E) from 0 to 90 parts by weight of a polyarylene ether or polar group modified polyarylene ether.

Syndiotactic vinylaromatic polymers especially include syndiotactic polystyrene prepared by coordination polymerization of styrene monomer under conditions to provide a high degree of syndiotacticity. Most highly preferred are those polymers containing greater than 50 percent syndiotacticity at a racemic triad. Such polymers are known in the art having been previously disclosed in, for example, US-A-4,680,353; US-A-4,959,435; US-A-4,950,724; and US-A-4,774,301. Preferred compositions according to the invention comprise from 50 to 90 parts by weight syndiotactic vinylaromatic polymer.

Rubbery polymers include any elastomeric polymer, that is, organic and inorganic polymers having Tg less than 25°C, preferably less than 0°C, and having the previously specified rubbery domain forming properties and melt flow rate. Examples of the types of polymers from which the present rubbery polymers are selected include homopolymers and copolymers of conjugated dienes, especially butadiene, and hydrogenated derivatives thereof, preferably polybutadiene, styrene/butadiene block copolymers, and hydrogenated polybutadiene; polymers of α -olefins, such as styrene grafted polyolefins, ethylene/propylene copolymers, and terpolymers of ethylene, propylene and a comonomer such as hexadiene or ethylidene-norbornene; acrylate polymers, such as polybutylacrylate, and polycyclohexylacrylate; grafted derivatives of the foregoing rubbery polymers such as polystyrene-, polymethylmethacrylate-

or styrene/methyl methacrylate copolymer-grafted rubbery polymers; and silicone polymers such as polysiloxanes. Preferred are high molecular weight styrene/butadiene/styrene triblock copolymers, especially hydrogenated derivatives thereof, also referred to as styrene/ethylene/butylene/styrene copolymers. Such polymers are conveniently prepared by anionic
5 polymerization techniques using difunctional initiators, by coupling of living diblock polymers made by monofunctional initiators or by sequential polymerization. Such processes are previously disclosed in the art and well known to the skilled artisan.

The rubbery polymers are suitably chosen in order to impart impact absorbing properties to the polymer composition. It is believed, without wishing to be bound by such
10 belief, that under the extreme temperatures required for compounding syndiotactic vinylaromatic polymers, most conventional rubbery polymers lose their structural integrity and do not form impact absorbing domains. Rather, the rubbery polymer becomes extended and drawn by the compounding forces into thin sections that are incapable of absorbing impact forces. This result is due to several factors including the viscosity properties of the
15 rubbery polymer and the matrix polymer (that is, the syndiotactic vinylaromatic polymer and optional polyphenylene ether) under the compounding conditions employed, the interfacial tension existing between the rubber phase and the matrix, and the extent of relaxation afforded the polymer melt. The first two factors are determined by the physical and chemical properties of the rubbery polymer and the matrix, whereas the latter factor is controllable by
20 the conditions utilized in the compounding or molding operation.

Generally, it is desirable to provide a rubbery polymer having extremely high melt viscosity, that is, very low melt flow. Such polymers having high melt viscosity are not drawn into extremely thin sections by the shear forces of the compounding process, and retain greater ability to reform discrete rubber particles more closely resembling spherical particles upon
25 discontinuance of shearing forces. Additionally, the molten rubbery polymer beneficially should retain sufficient elastic memory to reform droplets in the melt when shearing forces are absent. In satisfaction of this desirable property, the melt viscosity of the rubber should be relatively high compared to that of the matrix resin. Most preferred rubbers have a melt flow rate, Condition G, ASTM D-1238, from 0 to 0.5 g/10 min.

30 A second desirable characteristic of the present composition is that the compatibility of the rubbery polymer and the matrix polymer in the melt be selected so as to develop maximum interfacial tension between the molten phases consistent with the need for satisfactory adhesion between the solid phases to promote impact absorption. Increased interfacial tension in the melt promotes rubber droplet formation due to the driving force to
35 reduce surface area of the rubber particles in contact with the matrix. This increased interfacial tension in the melt does not necessarily result in incompatible, solid polymer phases that reduce impact strength in the molded part.

The operating conditions are preferably chosen to provide sufficient relaxation time in the melt so that the aforementioned rubber particle formation can occur. If the molten polymer, containing undesirable thin strata of the impact modifier due to shearing forces, is quenched relatively quickly from the melt, the necessary droplet formation cannot occur and the resulting molded part will be deficient in impact properties. This result can occur, for example, in a molding process using molds operating at too low a mold temperature.

Generally, higher molecular weight polymers possess increased melt viscosity. Accordingly, preferred rubbery polymers are those rubbers having Mw from 100,000 to 400,000 Daltons, more preferable from 150,000 to 300,000 Daltons, and having Tg less than 25°C, more preferably less than 0°C. Weight average molecular weights recited herein are apparent values based on a polystyrene standard, derived from gel permeation chromatography data, and not corrected for hydrodynamic volume differences between polystyrene and other polymeric components. Low molecular weight rubbery polymers, that is, polymers having molecular weight less than 100,000 Daltons, have been found to possess insufficient melt viscosity to achieve the desired rubber droplet formation. Preferred quantities of the rubbery polymer are from 2 to 30, most preferably 5 to 25 parts by weight. Also, hydrogenated styrene/butadiene/styrene triblock copolymers generally possess reduced melt flow rate compared to unhydrogenated polymers of the same molecular weight. Accordingly, hydrogenated styrene/butadiene/styrene triblock copolymers are preferred for use in the present invented blend.

Nucleators for use herein, are compounds capable of reducing the time required for onset of crystallization of the syndiotactic vinylaromatic polymer upon cooling from the melt. Nucleators provide a greater degree of crystallinity in a molding resin and more consistent levels of crystallinity under a variety of molding conditions. Higher levels of crystallinity are desired in order to achieve increased chemical resistance. In addition crystal morphology may be desirably altered. Examples of suitable nucleators for use herein are metal salts, especially aluminum salts of organic acids. Especially preferred compounds are aluminum salts of benzoic acid and C₁₋₁₀ alkyl substituted benzoic acid derivatives. A most highly preferred nucleator is aluminum tris(p-tert-butyl)benzoate. The amount of nucleator used should be sufficient to cause nucleation and the onset of crystallization in the syndiotactic vinylaromatic polymer in a reduced time compared to compositions lacking in such nucleator. Preferred amounts are from 0.5 to 5 parts by weight.

Surprisingly, in the present formulation it has now been discovered that the presence of both the specific impact absorbing domain forming rubber and the nucleator results in improved impact resistance as measured by Izod impact resistance. In the absence of a nucleator, a noticeable decrease in impact resistance is observed for the resin blends. In addition, distortion temperature under load, DTUL, is also increased by the presence of such a nucleator.

The reinforcing agent may be any mineral, glass, ceramic, polymeric or carbon reinforcing agent. Such material may be in the shape of fibers having a length to diameter ratio (L/D) of greater than 5, or in the shape of particulates having (L/D) less than 5. Preferred particle diameters are from 0.1 micrometers to 1 millimeter. Suitable reinforcing agents include mica, talc, glass microspheres, glass fibers, ceramic whiskers, carbon fiber strands, boron nitride fibers, and aramide fibers. Preferred reinforcing agents are glass fibers, glass roving or chopped glass fibers having lengths from 0.1 to 10 millimeters and L/D from 5 to 100. Two such suitable glass fibers are available from Owens Corning Fiberglas under the designation OCF 187A™ or 497™. The amount of reinforcing agent employed is preferably from 10 to 50 parts by weight.

The reinforcing agent may include a sizing agent or similar coating which, among other functions, may promote adhesion between the reinforcing agent and the polyarylene ether or polar group functionalized polyarylene ether. Suitable sizing agents may contain amine, aminosilane, epoxy, and aminophosphine functional groups and contain up to 30 nonhydrogen atoms. Preferred are aminosilane coupling agents and C₁₋₄ alkoxy substituted derivatives thereof, especially 3-aminopropyltrimethoxysilane.

Polyarylene ethers are a known class of polymer having been previously described in US-A-3,306,874; US-A-3,306,875; US-A-3,257,357; and US-A-3,257,358. A preferred polyarylene ether is poly(2,6-dimethyl-1,4-phenylene)ether. The polyphenylene ethers are normally prepared by an oxidative coupling reaction of the corresponding bisphenol compound. Preferred polyarylene ethers are polar group functionalized polyarylene ethers, which are a known class of compounds prepared by contacting polar group containing reactants with polyarylene ethers. The reaction is normally conducted at an elevated temperature, preferably in a melt of the polyarylene ether, under conditions to obtain homogeneous incorporation of the functionalizing reagent. Suitable temperatures are from 150°C to 300°C.

Suitable polar groups include the acid anhydrides, acid halides, acid amides, sulfones, oxazolines, epoxies, isocyanates, and amino groups. Preferred polar group containing reactants are compounds having up to 20 carbons containing reactive unsaturation, such as ethylenic or aliphatic ring unsaturation, along with the desired polar group functionality. Particularly preferred polar group containing reactants are dicarboxylic acid anhydrides, most preferably maleic anhydride. Typically the amount of polar group functionalizing reagent employed is from 0.01 percent to 20 percent, preferably from 0.5 to 15 percent, most preferably from 1 to 10 percent by weight based on the weight of polyarylene ether. The reaction may be conducted in the presence of a free radical generator such as an organic peroxide or hydroperoxide agent if desired. Preparation of polar group functionalized polyarylene ethers have been previously described in US-A-3,375,228; US-A-4,771,096 and US-A-4,654,405.

The polar group modified polyarylene ethers beneficially act as compatibilizers to improve adhesion between the reinforcing agent and the syndiotactic vinylaromatic polymer. Generally if less than 0.01 weight percent of the polar group containing reactant is employed in the preparation of the polar group modified polyphenylene ether, less than desired compatibility between the reinforcing agent and the syndiotactic vinylaromatic polymer resin is attained. If greater than 20 weight percent is employed, no significant advantage in polymer properties due to improved compatibility is realized. The amount of polyarylene ether employed in the present resin blend is beneficially from 0.1 to 50 parts by weight. For polar group modified polyarylene ethers used as a compatibilizer, the preferred quantity for use is from 0.1 to 10 parts by weight.

In one embodiment of the invention the polar group modified polyarylene ether may be in the form of a coating applied to the outer surface of the reinforcing agent to impart added compatibility between the reinforcing agent and the polymer matrix. The polar group modified polyarylene ether so utilized may be in addition to further amounts of polyarylene ether or polar group modified polyarylene ether also incorporated in the blend. The surface coating is suitably applied to the reinforcing agent by contacting the same with a solution or emulsion of the polar group functionalized polyarylene ether. Suitable solvents for dissolving the polar group functionalized polyarylene ether to form a solution or for use in preparing an emulsion of a water-in-oil or oil-in-water type include methylene chloride, trichloromethane, trichloroethylene and trichloroethane. Preferably the concentration of polar group functionalized polyarylene ether in the solution or emulsion is from 0.1 weight percent to 20 weight percent, preferably 0.5 to 5 percent by weight. After coating of the reinforcing agent using either a solution or emulsion, the liquid vehicle is removed by, for example, evaporation, devolatilization or vacuum drying. The resulting surface coating is desirably from 0.001 to 10 weight percent of the uncoated reinforcing agent weight.

The compositions of the present invention are prepared by combining the respective components under conditions to provide uniform dispersal of the ingredients. Alternatively, where a polar group modified polyarylene ether is used, this component of the blend may be prepared in situ by reacting the polar group reactant with the polyphenylene ether and further incorporating the molten product directly into the finished blend. Mechanical mixing devices such as extruders, ribbon blenders, solution blending or any other suitable device or technique may be utilized.

Additional additives such as blowing agents, extrusion aids, antioxidants, pigments, plasticizers, stabilizers, and lubricants, may also be included in the composition in amounts up to 10 percent, preferably up to 5 percent, by weight, based on final composition weight.

Desirably the resulting composition possesses an Izod impact resistance (ASTM D-256) of at least 2.5 ft lbs/in notch (130 J/M notch) and a DTUL (Distortion Temperature Under Load), ASTM D-648 @ 264 psi (1.8 MPa) of at least 200°C.

Having described the invention the following example is provided as further illustrative and is not to be construed as limiting. Unless stated to the contrary parts and percentages are based on weight.

Example 1

Blends of components identified in Table I were prepared by first dry mixing the respective components (excepting glass fibers) in a drum mixer. All blends additionally contained as antioxidant and thermal stabilizer 0.1 percent tetrakis(methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate))methane (Irganox 1010™) and 0.1 percent bis(2,4-di-tertbutylphenyl)pentaerythritol (Ultranox 626™). The resulting mixture was passed through a 40 mm W-P compounding extruder at a controlled rate while adding chopped fiberglass. The resulting compounded blend was injection molded under standard conditions and tested according to ASTM test methods. Results are contained in Table I.

Identification of components:

(A) Syndiotactic polystyrene (SPS): Mw = 400,000, Tg 95°C and Tm 270°C (available from The Dow Chemical Company as XU 72104.04).

(B) Rubber: Kraton G 1651™, hydrogenated styrene/butadiene/styrene block copolymer, Mw = 270,000, Mw/Mn = 1.06, styrene content 32 percent, melt flow (Condition X ASTM D-1238), 0 g/10 min. Tg = -48°C, available from Shell Chemical.

(C) Nucleator: aluminum tris(p-tert-butylbenzoate), available from Shell Chemical.

(D) Glass fibers: 0.125 in length x 0.009 in diameter (3 mm x 0.2 mm diameter), coated with 3-aminopropyltrimethoxysilane coupling agent. (Owens Corning Fiberglas 187A™).

(E) Maleic anhydride modified polyphenylene oxide resin (MAPPO): 3 weight percent maleic anhydride prepared by injecting maleic anhydride at an appropriate rate to provide the desired maleic anhydride content into a 0.8 in (2.0 cm) Welding Engineers Twin Screw extruder which is charged with poly(2,6-dimethyl-1,4-phenylene)ether and operated under conditions to melt plastify the resin. The resulting product is extruded and chopped into granules.

Table I

	<u>Run</u>	<u>SPS (%)</u>	<u>Rubber (%)</u>	<u>MAPPO (%)</u>	<u>Fiberglass (%)</u>	<u>Nucle-ator (%)</u>	<u>Impact¹ Strength</u>	<u>DTUL °C</u>
5	*	67.2	0.0	1.8	30	1.0	1.7 (91)	249
	1	59.4	9.0	1.8	30	0.6	2.6 (139)	224

* comparative

¹ notched Izod impact strength, ASTM D-256, ft-lbs/in notch (J/M notch)10 Example 2

The reaction conditions of Example 1 are substantially repeated excepting that the glass fibers used are precoated with a 4 percent solution of MAPPO in trichloroethylene and dried prior to compounding. Results are contained in Table II.

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Table II

	<u>Run</u>	<u>SPS (%)</u>	<u>Rubber (%)</u>	<u>MAPPO (%)</u>	<u>Fiberglass (%)</u>	<u>Nucle-ator (%)</u>	<u>Impact¹ Strength</u>	<u>DTUL °C</u>
20	2	59.4	10	0	30	0.6	2.7 (144)	240
	3	57.6	10	1.8	30	0.6	3.0 (160)	216

¹ notched Izod impact strength, ASTM D-256, ft-lbs/in notch (J/M notch)25 Example 3

The reaction conditions of Example 1 are substantially repeated excepting that the amount of SPS in the blend is 52.8 weight percent, the amount of Kraton™ rubber in the blend is 13.2 weight percent, the amount of Owens Corning OCF 497 glass fiber is 30 percent, and the MAPPO content is 3.0 percent of the total blend weight. Several comparative rubbers not having domain forming properties under the conditions tested were used. Results are contained in Table III.

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Table III

	<u>Run</u>	Rubber	<u>Impact Strength</u> ¹	<u>notched Impact Strength</u> ²	<u>Tensile Strength</u> ³	<u>Elongati n</u> (percent)	<u>Tensile Modulus</u> ⁴	<u>DTUL</u> (°C) ⁵
5								
	4	G1651	9.3 (12.6)	2.5 (3.4)	13.0 (8.9)	1.8	1.06 (7.3)	205
	A*	G1650 ⁶	6.7 (9.1)	1.3 (1.8)	9.9 (6.8)	1.8	0.78 (5.4)	115
	B*	G1652 ⁷	5.8 (7.9)	1.2 (1.6)	9.1 (6.3)	1.7	0.62 (4.3)	121
10	C*	G1657 ⁸	7.3 (9.9)	1.7 (2.3)	9.3 (6.4)	1.8	0.72 (5.0)	171

¹ Izod impact strength, ASTM D-256, ft-lbs (Joules)

² notched Izod impact strength, ASTM D-256, ft-lbs/in notch (J/M notch)

³ lb/in² x 10³ (MPa)

⁴ lb/in² x 10⁶ (GPa)

⁵ Distortion Temperature Under Load ASTM D-256, 264 lbs/in² (1.8 MPa)

* Comparative, not an example of the invention

15 ⁶ hydrogenated styrene butadiene triblock copolymer, Melt Flow Rate ASTM D 1238 Condition X = 29 g/10 min

⁷ hydrogenated styrene butadiene triblock copolymer, Melt Flow Rate ASTM D 1238 Condition X > 200 g/10 min

⁸ hydrogenated styrene butadiene triblock copolymer, Melt Flow Rate ASTM D 1238 Condition X > 800 g/10 min

As may be seen by reference to Table III, improved performance of the blend results from the use of a rubber meeting the requirements of good impact absorbing domain formation properties, especially a melt flow rate, Condition X of 0 to 0.5 g/10 min.

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Claims

1. A composition of matter comprising:
 - A) from 25 to 90 parts by weight of a syndiotactic, vinylaromatic thermoplastic resin,
 - B) from 1 to 50 parts by weight of a rubbery, impact absorbing, domain forming polymer, having a melt flow rate, Condition X (315°C, 5.0 Kg) from 0 to 0.5 g/10 min,
 - C) from 0.1 to 30 parts by weight of a nucleator for the syndiotactic, vinylaromatic thermoplastic resin,
 - D) from 0 to 90 parts by weight of a reinforcing agent, and
 - E) from 0 to 90 parts by weight of a polyarylene ether or polar group modified polyarylene ether.
2. A composition according to Claim 1, comprising:
 - from 50 to 80 parts by weight of A);
 - from 2 to 30 parts by weight of B);
 - from 0.5 to 5 parts by weight of C);
 - from 10 to 50 parts by weight of D); and
 - from 0.1 to 50 parts by weight of polyarylene ether or 0.1 to 10 parts by weight of polar group modified polyarylene ether.
3. A composition according to Claim 1 or Claim 2, wherein the rubbery polymer is a styrene/butadiene/styrene triblock copolymer.
4. A composition according to Claim 3, wherein the rubbery polymer is a hydrogenated styrene/butadiene/styrene triblock copolymer.
5. A composition according to any one of the preceding claims, wherein the rubbery polymer has an apparent weight average molecular weight from 100,000 to 400,000 Daltons (based on a polystyrene standard derived from gel permeation chromatography data and uncorrected for hydrodynamic volume difference).
6. A composition according to any one of the preceding claims, wherein the rubbery polymer has a Tg less than 0°C.
7. A composition according to any one of the preceding claims, wherein the rubbery polymer has a melt flow rate (Condition G) of 0 to 0.5 g/min.
8. A composition according to any one of the preceding claims, comprising from 5 to 25 parts of the rubbery polymer.
9. A composition according to any one of the preceding claims, wherein the nucleator is a metal salt.
10. A composition according to Claim 9, wherein the nucleator is an aluminum salt of an organic acid.

11. A composition according to Claim 10, wherein the nucleator is aluminum tris(p-tert-butylbenzoate).
12. A composition according to any one of the preceding claims, wherein from 0.5 to 5.0 parts by weight of the nucleator are present.
- 5 13. A composition according to any one of the preceding claims, comprising a polar group modified polyarylene ether.
14. A composition according to Claim 13, wherein the polar group modified polyarylene ether is a dicarboxylic acid anhydride modified polyarylene ether.
15. A composition according to Claim 14, wherein said anhydride is maleic
10 anhydride.
16. A composition according to any one of Claims 13 to 15, wherein the polar group modified polyarylene ether is produced by melting a polyarylene ether, contacting from 0.5 to 15 weight percent polar group functionalizing reagent with the molten polyarylene ether, and recovering the resulting product.
- 15 17. A composition according to any one of Claims 13 to 16, comprising from 0.1 to 5 parts by weight polar group modified polyarylene ether.
18. A composition according to any one of the preceding claims, wherein at least part of the polar group modified polyarylene ether is present as a surface coating in the reinforcing agent.
- 20 19. A composition according to any one of the preceding claims, wherein the syndiotactic vinylaromatic polymer is syndiotactic polystyrene containing greater than 50 percent syndiotacticity at a racemic triad.
20. A composition according to any one of the preceding claims, wherein the reinforcing agent comprises glass fibers.
- 25 21. A composition according to any one of Claims 1 to 17, 19 and 20, wherein the reinforcing agent additionally comprises a sizing composition on the surface thereof.
22. A composition according to Claim 21, wherein the sizing agent is an aminosilane functional compound.

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INTERNATIONAL SEARCH REPORT

Intern: Application No
PCT/US 94/00790

A. CLASSIFICATION OF SUBJECT MATTER

C 08 L 25/06, C 08 L 71/12, C 08 L 53/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 08 L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A2, 0 356 857 (IDEMITSU KOSAN COMPANY LTD.) 07 March 1990 (07.03.90), page 3, line 27 - page 4, line 29; page 5, lines 19-36; page 6, lines 14-21; examples; claims.	1-8, 19-22
A	---	9-18
A	EP, A1, 0 382 064 (IDEMITSU KOSAN COMPANY LTD.) 16 August 1990 (16.08.90), page 2, lines 5-37; page 11, line 43 - page 12, line 12; examples; claims.	1-8, 13-22
X	---	9-12
A	EP, A1, 0 380 968 (IDEMITSU KOSAN COMPANY LTD.)	1-22

☐ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.

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01.06.94

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European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>08 August 1990 (08.08.90), page 3, line 24 - page 4, line 54; examples; claims. --</p> <p>US, A, 4 866 129 (BRANDSTETTER et al.) 12 September 1989 (12.09.89), totality. ----</p>	1-22

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
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ANNEXE

au rapport de recherche inter-
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PCT/US 94/00790 SAE 85898

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